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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08J 3/00, C08K 3/20, 5/01 C08L 95/00, 91/08	A1	(11) International Publication Number: WO 92/18558 (43) International Publication Date: 29 October 1992 (29.10.92)
(21) International Application Number: PCT/US92/02800 (22) International Filing Date: 10 April 1992 (10.04.92) (30) Priority data: 684,231 12 April 1991 (12.04.91) US (60) Parent Application or Grant (63) Related by Continuation US 684,231 (CIP) Filed on 12 April 1991 (12.04.91) (71) Applicant (for all designated States except US): ROBERT M. EVANS ASSOCIATES, INC. [US/US]; 1365 Forest Hills Blvd., Cleveland Heights, OH 44118 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : EVANS, Robert, M. [US/US]; 1365 Forest Hills Blvd., Cleveland Heights, OH 44118 (US). XIAO, Han, X. [CN/US]; 26170 Kiltartan, Farmington Hills, MI 48018 (US). FRISCH, Kurt, C. [US/US]; 17986 Parke Lane, Grosse Isle, MI 48138 (US). (74) Agents: BRENNAN, Michael, P. et al.; Harness, Dickey & Pierce, P.O. Box 828, Bloomfield Hills, MI 48303 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>
(54) Title: POLYURETHANE-CONTAINING SEALANT AND COATING (57) Abstract <p>By way of summary, the present invention relates to waterborne coating compositions, methods of preparing such compositions, and methods of applying such compositions. More particularly, but without limitation, two compositions of the present invention comprise water-containing dispersions, suspensions or emulsions employing either (a) about 10 % to about 90 %, by weight of the final compositions, of a select urethane-urea dispersion; having incorporated therein either (b) about 10 % to about 90 %, by weight of the final composition, of a bituminous material, such as asphalt or (c) about 10 % to about 90 %, by weight of the final composition, of a (vinyllic) latex material. An additional water-containing dispersion, suspension or emulsion is disclosed without limitation, as employing (a) about 5 % to about 10 % by weight of the final composition of a urethane-urea dispersion; (b) about 5 % to about 30 % by weight of the final composition of a (vinyllic) latex material; and (c) about 10 % to about 90 %, by weight of the final composition, of a bituminous material, preferably asphalt.</p>		

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POLYURETHANE-CONTAINING SEALANT AND COATING

This application is a continuation-in-part of U.S. Serial Number 684,231,
5 filed April 12, 1991 and which is expressly incorporated herein by reference.

This application is related to compositions and methods providing improved
sealing and coating properties. Such compositions and methods are particularly useful in
sealing and/or coating aging, chalky, rough or powdery surfaces which are typically difficult
to seal or coat and maintain good adhesion, such as roofs or driveways. They are also
10 particularly useful in coating flexible surfaces (or surfaces undergo thermal
expansion/contraction) and require the associated coating to flex without significant loss
of its sealing properties.

BACKGROUND OF THE INVENTION

15 The compositions and methods of the present invention relate to
waterborne sealing or coating compositions which employ urethane-urea dispersions.
They also relate to compositions which include urethane-urea dispersions ("UUD") and
which also employ asphalt, natural and/or synthetic latex, or mixtures of all three, and may
additionally employ other select additives or components. These other additives or
20 components include other polymers or polymer-like material (e.g., in addition to latices
and asphalt emulsions); pigments; fillers; biocides; antioxidants; and the like.

Similar compositions and methods are known in the art; however, none of
the art-disclosed compositions or methods provide the same combination of unique
properties and advantages as the compositions and methods of the present invention.

25 For example, Warach, in "Polyurethane Dispersions - Waterbased High
Performance Adhesive Material," Polymeric Materials Science and Engineering, Vol. 61,
Fall, 1989, published by the American Chemical Society, discusses the manufacture of

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polyurethane dispersions, including those blended with vinylacetate/ethylene; vinylacetate; acrylic; and natural rubber (latex); as an adhesive. No mention is made of the inclusion of asphalt, or the importance of particle size when employing UUD as a sealant coating.

U.S. 3,967,012, issued June 26, 1976 to Ebner, discloses a process for
5 applying a coating to a surface by employing an aqueous suspension or dispersion selected from the group which consists of bitumens, asphalts, and tars; and moisture-resistant natural or synthetic rubbers or synthetic resin particles. The patentee further indicates that the primary coating substances may include one or more of the mentioned classes of compound such as a polymethyl methacrylate latex in which particles of polystyrene or a
10 prepolymer of the urethane type are dispersed together with bitumen particles and/or a natural or synthetic (ABS-type) rubber. However, such compositions must be heated after being applied to the surface to effect coagulation to form a coherent layer (while at the same time avoiding "material evaporation of water therefrom"); and lastly then heated to dry the coagulated composition.

15 U.S. Patent No. 4,160,065, (expressly incorporated herein by reference) issued July 3, 1979 to Leowrigkeit et al. The patentee discloses specific latex materials and, more specifically, water-dispersible polyurethane products from stable latices of select chain-extended quaternized polyurethane ureas. In summary, a specific latex is made from a quaternized isocyanate terminated prepolymer. These materials are disclosed as being
20 useful as adhesives and "skin-coat" films and do not require heat for "drying."

U. S. Patent Nos. 3,873,484 issued to Bluestein et al. on March 25, 1975; and 3,758,427 issued to Katsibas on September 11, 1973; are directed to additional water-dispersible polyurethanes. Both of these patents are expressly incorporated herein by reference.

25 U. S. Patent No. 4,186,118, issued to Reischl et al. on January 29, 1980, discloses a process for preparing modified aqueous synthetic resin dispersions which

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includes introducing organic diisocyanates (which are liquid at room temperature) into polyurethane-containing, non-sedimenting, aqueous synthetic resin dispersions. The resulting aqueous dispersions so modified are described as containing latex particles which are enveloped with polyurea formed from the diisocyanates. The resulting compositions
5 are described as being useful as water-resistant surface coatings. This reference suggests that aqueous dispersions of non-polyurethane polymerization products may be mixed with the polyurethane dispersion before the process described by the patentee is carried out. Polymer latices can be made from, among other materials: natural or synthetic rubber; butadiene-methacrylate copolymers; polyacrylic acid esters; PVC; and others. See, without
10 limitation, Col. 2, lines 34-44.

U. S. Patent No. 3,988,278 issued to D. C. Bartizal on October 26, 1976 discloses self-emulsified polyurethane polyurethane-polyurea latices formed by chain extending (in water) a prepolymer which contains about two isocyanates group (per molecule) at the ends of a chain. Attached to some of these prepolymer chains is a
15 pendant group; at the end of the pendant group is either a "salt-forming" group or a hydrophilic group. It is the patentee's contention that it is the inclusion of these latter groups which produces the resulting self-emulsified characteristics.

U. S. Patent No. 3,796,678, issued to D.C. Bartizal on March 12, 1974, discloses modified polyurethanes for pressure-sensitive adhesives.

20 U. S. Patent No. 3,962,167, issued to R. Martorano et al. on June 8, 1976, discloses aqueous coating compositions which are primarily thermosetting compositions.

U. S. Patent No. 4,002,004, issued to D. C. Cavin on January 11, 1977, discloses cationic emulsion which contains asphalt.

See also (for anionic urethane-urea materials) U.S. 3,759,873; 3,882,189;
25 3,945,899; 4,046,729; 4,163,094; and 4,554,308; for nonionic urethane-urea materials see

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U.S. 4,403,083; 4,501,852; and 4,472,550. U.S. 4,046,729 is particularly useful for guidance in preparing useful anionic materials.

SUMMARY OF THE INVENTION

5 The present invention relates to novel waterborne coating and/or sealing compositions, methods of preparing such compositions, and methods of applying waterborne coating compositions. More particularly, but without limitation, exemplary coating or sealing compositions of the present invention comprise dispersions or suspensions preferably employing: (a) a select urethane-urea dispersion at a level of up
10 to about 90% by weight of solids of the final compositions (wherein said UUD is preferably a chain-extended anionic, cationic and nonionic polyurethane-urea dispersion and is optionally a UUD modified latex) wherein the UUD preferably has an average particle size of less than about 0.1 microns, more preferably less than about 0.65 and still more preferably about 0.02 to about 0.06 microns; and (b) up to about 90%, by weight
15 of solids of the final composition, of a bituminous material, preferably as asphalt added as an asphalt emulsion or natural latex. The final material, when applied, preferably cures at ambient temperatures and without applying heat. Other exemplary preferred compositions of the present invention also comprise (a) about 3% to about 40%, by weight of solids, of a urethane-urea dispersions having a select average particle size; (b)
20 about 3% to about 30% of a natural or synthetic latex material; and (c) about 10% to about 94% of a bituminous material (preferably an asphalt emulsion) wherein said composition cures without application of heat. The resulting compositions are useful (without limitation) as roofing or driveway coating and sealing, coating and membrane-forming materials when allowed to air dry at ambient temperatures.

25 The methods of the present invention also include the application of a composition comprising a blend of a urethane-urea dispersion (UUD) with a select

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average particle size. The methods further include the application of a natural or synthetic latex (e.g., an acrylic) modified by the inclusion of a UUD. The methods still further include the application of an asphalt modified by a UUD or UUD/latex or UUD/latex/asphalt composition to a roof or driveway, preferably with the addition of a pigment, filler, or the like. The methods of the present invention also relate to the preparation of these materials and the application of these compositions to a surface in need of coating or sealing.

DETAILED DESCRIPTION OF THE INVENTION

10 Urethane-urea dispersions (UUD) based upon or which employ aromatic isocyanates, aliphatic isocyanates (including cyclic aliphatics), trimeric isocyanates, or mixtures thereof, are useful in the compositions and methods of the present invention. Aliphatic-based materials, and more particularly cyclic aliphatic-based materials, are highly preferred. Such art-disclosed teachings of these compositions are included in *Waterborne*
15 *Polyurethanes*, J. W. Rosthauser and K. Nachtkamp, published as part of a collection in *Advances in Urethane Science and Technology*, Kurt C. Frisch and D. Klempner, Technomic Publishing, Vol. 10; 1987 pp. 121-162, and incorporated herein by reference.

Another useful discussion of the chemistry and application of aqueous polyurethane can be found in the *Polyurethane Handbook*, ed. G. Oertel, Hanser
20 Publishers, Carl Hanser Verlag, Munich, Germany, (1985).

A wide variety of useful water-dispersible urethane-urea products are well known. Preferred materials include those described in Warrach and U.S. Patent Nos. 3,873,484; 3,750,427; 4,046,729; 4,403,083; 4,501,852; and 4,472,550, discussed above and expressly incorporated herein by reference. See also Examples A-1 through A-6, herein,
25 for preferred anionic materials.

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In a highly preferred embodiment, the anionic, cationic or nonionic urethane-urea is modified by the inclusion or addition of a latex.

In general, these urethane-urea dispersions useful in the present invention are prepared by fully reacting urethane polymers in an aqueous system. They may be
5 cationic, anionic or nonionic, depending upon the selection of the functional diol employed.

In general, a polyol, a diisocyanate, a functional diol, a neutralizing agent (if necessary), a chain extender, and water are employed; the resulting products are fully reacted. While anionic, cationic and nonionic materials are useful, anionic materials are
10 presently highly preferred.

It should be noted that the following description will at times focus upon the production of cationic materials due to their suitability to serve as a model for the preparation of UUD components of the present invention. However, this is done merely for convenience; as noted above, the anionic materials (e.g., as depicted in the Examples
15 A-1 - A-6) are preferred. The skilled artisan will appreciate that this description may be varied to arrive at an anionic or nonionic UUD.

In accordance with the preferred compositions and process of the present invention, the NCO-terminated anionic, cationic or nonionic prepolymer is dispersed in water to provide a dispersion of an NCO-terminated prepolymer. The polyurethane
20 dispersion further reacts with an amine-reactive reagent to form the desired chain extended polymeric product having a higher molecular weight. Preferably, the amine-reactive reagent is added substantially together with the water.

Liquid polymers based on butadiene and containing a controlled number of hydroxyl functional groups can be utilized for the preparation of the prepolymer used
25 in the present invention. Preferably, a hydroxylated polybutadiene having a functionality of about 2.1 is used.

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The polyol or mixture of polyols utilized for the preparation of such a prepolymer for use in the present invention preferably has a hydroxyl number in the range of from about 10 to about 200, most preferably in the range of from about 20 to about 80 and optimally from about 30 to about 60, and is preferably a diol or a triol, most
5 preferably an alkoxyated ether diol.

The polyol can also comprise, alternatively, a hydroxyl or polyhydroxy-containing polyester. Such a compound preferably comprises a dihydroxy or a trihydroxy compound and, optimally, the dihydroxy polyester polyol is utilized.

Polyether type polyols are most commonly derived from simple alkane
10 diols, polymerized by reaction with an alkylene oxide, for example, to form the corresponding polyoxyalkylene polyether polyols. The preferred polyol monomers can be selected from among the glycols, such as neopentylglycol, ethyleneglycol, diethyleneglycol, hexamethyleneglycol, 1,4- and 1,3-butyleneglycols, 1,3- and 1,2-propyleneglycols, and the corresponding dipropyleneglycols. The most useful monomeric triols include the alkyl
15 triols, such as trimethylolethane, trimethylolpropane, 1,2,4-butanetriol, 1,2,6-hexanetriol, glycerol, and triethanolamine. Aromatic polyols can also be used, such as trihydroxymethyl benzene. The alkylene oxides used in preparing the polyether polyols are preferably those which contain from two to about four carbon atoms, including, for example, ethylene oxide, 1,2-propylene oxide and 1,2-butylene oxide, and homopolymers and copolymers
20 thereof. The polyhydric, polyalkylene ether can also be prepared from reagents such as glycidol and cyclic ethers, such as tetramethylene ethers, and the epihalohydrins, e.g., epichlorohydrin. The polyaralkylene ether polyols are derived from the corresponding aralkylene oxides, such as, for example, styrene oxide, alone or mixed with alkylene oxide. Generally, 1,2-propylene oxide, and mixtures of 1,2-propylene oxide and ethylene oxide,
25 are preferred for the preparation of the polyether polyol reactant. The polyether polyols are useful in the present invention preferably at a molecular weight of from about 500 to

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about 8,000, most preferably from 1,000 to about 6,500, and optimally not greater than about 5,000, and are preferably characterized by a hydroxy functionality of at least about 1.5 up to about 8, and more preferably an average hydroxy functionality of from about 2 to about 5. Mixtures of all of the above may also be employed.

5 Generally, the polyester polyol compounds useful for preparing the prepolymer in accordance with the present invention, can be prepared by, for example, the reaction of a polyhydric alcohol with a polycarboxylic acid, generally each containing from about two to twenty carbon atoms. The polycarboxylic acid can be not only the free carboxylic acid, but such acid precursors as the corresponding acid anhydrides or acid
10 halides or even, for example, alkyl esters. The preferred acids are the dicarboxylic acids containing from about 4 to about 12 carbon atoms. Examples of the preferred carboxylic acid components include, for example, aromatic acids such as phthalic acid, terephthalic acid, isophthalic acid, tetrachlorophthalic acid; cycloaliphatic acids, such as dimerized linoleic acid, maleated and fumarated rosin acids, and cyclohexane-1,4-diacetic acid; but
15 preferably include the aliphatic acids, such as oxydipropionic, succinic, glutaric, adipic, azelaic, suberic, and sebacic acids, or mixtures of such acids. Lactones which can be used in place of the polyester polyols include those derived from gamma-butyrolactone, or epsilon-caprolactones. The glycols which can be utilized in the preparation of the prepolymer polyesters include any of those set forth above for the preparation of the
20 polyether polyols. Generally, however, a dihydric polyol is preferred when preparing the polyester even more than when preparing the polyether polyol.

 The polyester polyol reactants preferably have a molecular weight of at least about 500 and optimally between about 2,000 and 6,000. Generally, the maximum molecular weight for both the polyether and the polyester polyols is limited primarily by
25 the difficulty of mixing such materials with the other ingredients in the procedure. Thus, the higher molecular weight ingredients are useful, but because of the difficulty of working

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with them, they are not considered economical or practical and, therefore, are less preferred. An efficient mixing apparatus must be provided when dealing with such high molecular weight materials.

Other useful polyols are those based upon various saturated and
5 unsaturated hydrocarbons such as poly b d R-445HT; R65M (both available from Sartomer, Inc.); LIR-503 (KL-5) available from Kuraray Co., Ltd.). They can be employed in any of the anionic, cationic or nonionic UUDs. Likewise, polyols modified by grafting styrene and an acrylonitrile, such as Pluracol 637; Pluracol 1002; or Pluracol 1028 (all available from BASF Corp.) can also be employed in the preparation of a UUD.

10 The organic polyisocyanates useful in preparing the prepolymer compound in accordance with the present invention include those which contain at least two isocyanate groups per molecule, and may contain two or three isocyanate groups. The useful isocyanates include, aromatic, aliphatic, cycloaliphatic, and trimeric isocyanates. Most preferably a diisocyanate is utilized. Suitable organic polyisocyanates include, for
15 example, n-butylene diisocyanate, methylene diisocyanate, m-xylylene diisocyanate, p-xylylene diisocyanate, cyclohexyl-1,4-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3-(alpha-isocyanatoethyl)-phenyl isocyanate, 2,6-diethylbenzene-1,4-diisocyanate, diphenyl-dimethylmethane-4,4'-
diisocyanate, ethylidene diisocyanate, propylene-1,2-diisocyanate, cyclohexylene-1,2-
20 diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,5-naphthalene diisocyanate, diphenylmethane diisocyanate, 1,6-hexamethylene diisocyanate and isophorone diisocyanate, etc.

25 The aromatic, aliphatic diisocyanates and the cycloaliphatic diisocyanates are preferred. The diisocyanates which have been found most useful in the preparation

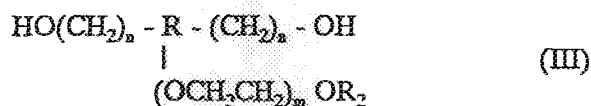
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of the prepolymers are, specifically, cycloaliphatic isocyanates, such as dicyclohexyl methane 4,4' diisocyanate (H_{12} MDI), isophorone diisocyanate (IPDI), and aromatic isocyanates including toluene diisocyanate (TDI), and diphenyl methane diisocyanate. IPDI based UUD's tend to have different characteristics than H_{12} MDI based UUD's. For example, IPDI-based materials appear to demonstrate improved elongation and adhesion with the H_{12} MDI-based materials appear to demonstrate better tensile strength.

When an anionic material is desired, the polyol and polyisocyanate are preferably reacted with an acid functional diol to form a pendant acid-containing NCO-terminated prepolymer. The preferred acid-containing diols may be of the formula
 10 $(HO)_xR(COOH)_y$ or $(HO)_xR(SO_3H)_y$, where R represents a straight or branched chain hydrocarbon radical having from 1 to about 20 carbon atoms, and preferably about 2 to about 5 carbon atoms; x represents a value of from 1 to about 5, and preferably about 2 to 3; and y represents a value of from 1 to about 4, and preferably 1 to about 3.

When such acid containing diols are employed, they may be neutralized
 15 (the pendent group) with organic or inorganic bases such as ammonium hydroxide, sodium hydroxide, potassium hydroxide, triethylamine, dimethylethylamine, and the like.

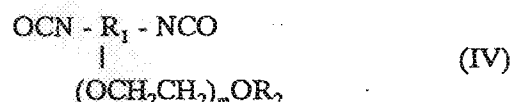
When a nonionic material is desired, the polyol and polyisocyanate described above may be reacted as described above except that a hydrophilic group-containing diol or diisocyanate may be employed in place of the diols. Useful hydrophilic-
 20 group containing materials are preferably ethoxylated materials of the formula III or IV



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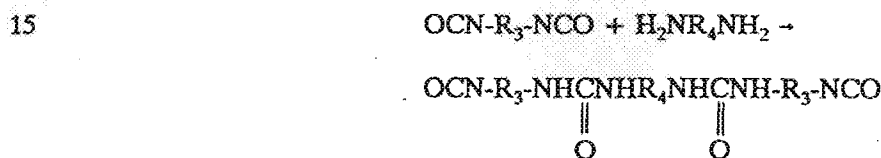
or

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5 wherein R represents a straight or branched chained hydrocarbon radical containing 1 to about 20 carbon atoms, and preferably about 2 to about 5 carbon atoms; n represents a value of from 1 to about 5, and preferably about 2 to about 3; m represents a value of about 1 to about 50, and preferably 2 to about 20, and even more preferably about 2 to about 10; R₂ represents a straight or branched hydrocarbon radical containing 1 to about 5 carbon atoms, preferably 1 to about 3; and R₁ represents either an aromatic or aliphatic hydrocarbon, e.g., H₁₂MDI, IPDI, etc.

The nonionic UUD can also be formed by reacting the prepolymer with diamines such as hydrazine and ethylene diamine, among others. For example:



20 wherein R₃ is an aromatic or aliphatic hydrocarbon, preferably H₁₂MDI or IPDI; and R₄ is (CH₂)_x wherein x is 0 to about 4. Continued chain growth then proceeds.

A neutralization step, typically required with the preparation of an anionic or cationic (quaternized) material, is not required with the preparation of a nonionic
25 UUD.

Generally, in carrying out the urethane prepolymer reactions, the only significant groups in the reactant compounds are the isocyanate groups and the hydroxyl groups which are reactive therewith. Any other group can be present in the reactants or in the final urethane polymer, so long as the group does not adversely interfere with, and
30 is preferably inert to, the desired isocyanate/hydroxyl reaction as well as the optional neutralizing reaction and the subsequent chain-extending reactions between the

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prepolymer and the amine-reactive reagent. Thus, acyclic, alicyclic, aromatic and heterocyclic groups can all be present on any of the reactive compounds as long as they do not adversely interfere. Similarly, inert substituent groups, such as certain halogens, can be present as long as they do not interfere with any of these reactions.

5 When desired in the preparation of a cationic material, any suitable monofunctional quaternizing agent can be utilized in preparing a prepolymer. A di(loweralkyl) sulphate is preferred. The lower alkyl groups most preferably contain up to about 6 carbon atoms each and include, for example methyl, ethyl, n-propyl, isopropyl, etc. Dimethylsulphate is most preferred because of its ready availability and low cost.

10 A catalyst is generally preferably present to increase the rate of reaction, especially between the polyisocyanate and the polyol. Catalysts which are useful for this reaction are well known in the art and include, for example, metal catalysts such as tin compounds and bismuth compounds, as well as other metal compounds, such as compounds of cobalt, lead, and, vanadium. Most preferred are the tin compounds, which
15 include the stannous salts, e.g. stannous octoate, stannous acetate, and stannous oleate, the stannic salts, e.g. stannic diacetate, and stannic di-octoate, and also the covalently-linked, so-called organotin compounds, such as the dialkyltin dicarboxylate salts, including, for example, dibutyltin diacetate, and dibutyltin dilaurate, and tributyltin oxide.

 The preparation of the prepolymer and the anionic, cationic or nonionic
20 isocyanate terminated prepolymer, as described above, is conventional in the art, and the various materials useful for forming such a prepolymer are generally described in the literature, for example, in the text *Advances in Polyurethane Science and Technology*, Vol. 10, Roshauser and Nachcamp; published by Technomic Publishing, (1987); also see Warrach as well as U. S. Patent Nos. 3,873,484, 4,046,729, 4,160,065, 4,403,083, 4,501,852,
25 and 4,472,550, all mentioned supra and incorporated herein by reference.

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The prepolymer is generally prepared in an anhydrous medium, and can include the presence of an inert diluent or solvent medium. The presence of solvent is optional, and can be avoided if the viscosity (if liquid) of the various reagents permits. Generally, not more than about 10% of an organic solvent is utilized, if any. Any suitable inert organic solvent can be utilized, and the term "inert" in this context refers to an ingredient which does not enter into, nor interfere with, the course of the prepolymerizing or quaternizing reactions. Useful such solvents include, preferably, n-methyl pyrrolidone, acetone and other water-soluble materials. Other useful solvents include, for example, tetrahydrofuran, dimethylformamide, ethylacetate, benzene, dioxane, and the like.

10 The solvent most preferably has a boiling point in the range of from about 40° to about 90°C, in order to facilitate separation of the solvent from water.

The proportions of the polyisocyanate reactant to the polyhydric alcohol reactant, including one or more polyols, can be varied to achieve desired results by varying the NCO/OH ratios in order to obtain different concentrations of soft and hard segments.

15 In preparing the prepolymer, generally the total isocyanate ($-NCO$) equivalent-to-total hydroxy equivalent, should be such as to provide from about 1.6 to about 2.4 equivalents of the hydroxy to about 3 to about 7 equivalents of the isocyanate, the preferred ratio being approximately 1.4 hydroxy equivalents to 2.1 isocyanate equivalents. Preferably, the proportions of the major reagents in the cationic prepolymer reaction mixture would be

20 as follows:

- (a) polyol about 0.8 to about 1.2 equivalents;
- (b) N-alkyl dialkanolamine about 0.8 to about 1.2 equivalents;
- 25 (c) polyisocyanate about 3 to about 5 equivalents; and
- (d) dialkylsulfate about 0.4 to about 0.6 equivalents.

The isocyanate terminated prepolymer, in accordance with the present

30 invention, comprises a terminal isocyanate group ($-NCO$) group content within the range

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of from about 0.5% to about 10% by weight, and most preferably in the range from about 1.4% to about 3.5% by weight of the isocyanate group.

As stated above, the prepolymer is generally prepared in anhydrous medium. The addition of a solvent, as explained above, is optional and depends upon the viscosity and state of the various reagents utilized and the apparatus which is available for carrying out the process. The reaction is generally carried out at a temperature above typical room temperatures, as the result of the reaction exotherm. However, the reaction can be carried out at a temperature of from about a typical room temperature (or even lower) up to the natural exotherm temperature of the reaction, which should generally be maintained at or below about 125°C, and preferably at no greater than about 85°C. Higher temperatures can be utilized but are not preferred because of possible concurrent side reactions at higher temperatures.

The reaction is generally initiated by admixing the polymeric polyol, such as the polyether polyol or polyester polyol, with an acid functional diol or tertiary alkanolamine or hydrophilic group containing diol and the polyisocyanate. Following substantial completion of this reaction, and cooling to almost room temperature, the prepolymer is by the addition of the neutralizing agent, for example, the triethylamine. In a preferred embodiment for preparing the present prepolymer about one equivalent weight of a diol, such as a polyoxyalkylene glycol, is admixed with about one hydroxyl equivalent of an acid functional diol, or N-alkyl dialkanolamine, or hydrophilic group-containing diol and about four equivalents of an organic polyisocyanate, most preferably, a diisocyanate. The resultant reaction mixture is then neutralized (if desired) with about 0.5 equivalent of a neutralizing agent, such as triethylamine.

The resulting anionic, nonionic or cationic (quaternized) prepolymer, as finally prepared, generally has an average molecular weight in the range of from about 500 to about 100,000; however, the molecular weight of the prepolymer is estimated and does

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not form a critical part of the present invention. It is prepared such that the typical or average particle size is in the range of from about less than 1 micron; more preferably less than about 0.8 microns; still more preferably less than about 0.65 microns, and still more less than about 0.4 microns. In one highly preferred embodiment, the average particle
5 size is in the range of about 0.02 to about 0.06 microns.

As noted above, the resulting UUD may then be employed to coat and/or seal an aging, chalky, rough and/or powdery surface. It is particularly useful in coating pavement or roofing surfaces. It is also useful in coating metal and plastic surfaces; "rubbery" surfaces such as some roofs; asphalt and concrete pavements; as a "cold patch"
10 mixture or to coat same; and to underbodies; etc.

The UUD, with the select particle size described above, may also be used to modify a waterborne latex-containing composition, or water-borne asphalt-containing composition; it may also be used to modify a latex-containing composition which is then employed to in turn modify a water-borne asphalt-containing composition.

15 These compositions are likewise useful in coating and/or sealing an aging, chalky, rough, powdery and/or flexible surface in need of such coating or sealing, particularly roofing and pavement surfaces.

Other surfaces which are particularly well suited for coating in accordance with the instant application include, without limitation, metals, woods, concrete, and
20 plastics, etc.

It has been observed that employing these UUDs (at the selected particle size) to modify other coating or paving composition, e.g., asphalt or latex compositions, even at very low levels, results in fairly dramatic improvements in performance of the composition so modified. While minimum levels of UUD of about 5 to about 10 percent
25 (by weight of solids) are preferred, levels as low of about one-half (1/2) to one percent (1%) by weight have been demonstrated to be extremely effective in certain environments.

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An asphalt emulsion, which can be anionic, cationic or nonionic, is added to the UUD prepared as described above to prepare the UUD/asphalt compositions of the present invention. The asphalt can be added to the waterborne urethane-urea systems described above (with or without modification with latex) by any conventional manner.

5 A number of commercial asphalt emulsions on the market may be employed to prepare such composition. When the asphalt emulsion is cationic, the pH should be adjusted with a base material such as triethanolamine or ammonium hydroxide to increase the pH value to greater than 7, and preferably between about 8 and 10 before addition. If the asphalt is anionic the pH must generally be higher than 7. A "neutral" asphalt emulsion generally
10 has a pH of about 7. Both high penetration and low penetration asphalt may be employed.

Simple admixing with the urethane-urea will generally suffice. It is preferred that the asphalt be added in the following method. The asphalt emulsion is slowly added to a container to which the UUD (or UUD/latex blend as described below)
15 has been previously added. The mixing is carried out under a medium agitation until the addition of asphalt emulsion is finished and a homogeneous mixture is formed. The weight ratios of the UUD (or UUD/latex blend) to the added asphalt emulsion is preferably from about 5% to about 95%, more preferably about 5% to about 50%; still more preferably about 5% to about 30%; and still more preferably about 10% to about
20 30%; by weight of total solids; but again, lower levels of the UUD or UUD/latex blend may be employed, e.g., as low as one-half (1/2) to one percent (1%) weight by total solids. A defoamer may be employed at a level of 0.1% to about 5% and preferably about 0.3% to about 2%, based upon total solids. The defoamer is added with slow agitation to release air bubbles before finishing the preparation of the modified asphalt emulsion.
25 Pigments, thickening agents, and anti-oxidants are optionally employed.

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As used herein, the term asphalt includes all useful bituminous materials; useful material can be substantially any pyrogenous distillate or tars composed mainly of hydrocarbons with small or trace amounts of heterocyclic compounds containing sulfur, nitrogen, oxygen, and the like. Such materials may be selected from the group consisting of straight run asphalt, air-blown asphalt, cracked asphalt, and mixtures thereof. Particularly preferred are asphalt emulsions manufactured by Koch Material Company under the tradename 5980; other similar materials are useful.

A typical formula for an anionic asphalt emulsion with a medium setting rate which would be used as a topcoat according to the present invention is as follows:

10	180-200 penetration asphalt	65.0
	Water	34.1
	Tall Oil (crude)	0.4
	Vinsol resin	1.4
	Sodium Hydroxide	0.09

15

A fast setting grade would have the following formula:

	180-200 penetration asphalt	65.0
	Water	34.6
20	Tall Oil (crude)	0.4
	Sodium Hydroxide	0.04

These components would be dispersed in any one of a variety of colloid mills, all of which work on the same basic principle -- a high speed rotor moving within a fixed stator. Openings can vary between .005 and .030 inches. The speed is between 1000 and 6000 revolutions per minute. A description of such a mill is shown in U.S. Patent 2,260,834.

The tall oil is added to a sodium hydroxide solution in the water. The mixture is heated with agitation until the tall oil dissolves in the sodium hydroxide solution to form the soap.

The asphalt is then heated until its viscosity is less than 300 seconds Saybolt Furol. The two phases -- the heated asphalt and the soap solutions -- are added

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to the face of the mill. The emulsion is formed in the mill by the high shearing forces. Particle size will be approximately 4 microns.

The more important properties of UUD modified asphalt emulsions are tensile strength, elongation, and retention of elongation at low temperatures. It has been
5 observed that if tensile strength of the UUD/asphalt emulsion composition is important, a UUD with a high hard segments percentage should be employed. Conversely, if elongation is more important, a UUD with a low hard segments percentage should be employed.

The UUD can be used to prepare some additional novel compounds, in
10 which UUD will be blended, preferably prior to the addition of asphalt, with various vinylic latices in a container equipped with an electrical stirrer at room temperature. A range of different ratios (by weight of solids) may be employed. For example 1 to 90, and preferably 10 to 90 parts of an anionic, cationic or nonionic UUD may be blended with 90 to 10 parts of various vinylic latices. More preferably, a ratio of about 30 parts to
15 about 50 parts of UUD (by weight of solids) is employed. In order to avoid phase separation or other precipitations, the pH value of the UUD modified latices added should be higher than 7, and preferably between about 8 and 10. The mixing process is carried out in a suitable container until a homogenous uniform blend is formed. As will be appreciated by the skilled artisan, the final composition can be characterized and
20 evaluated by solids content, viscosity, tensile strength, elongation, glass transition temperature, or low temperature flexibility properties. The asphalt emulsion is then added to the UUD modified latex as described above for the UUD.

The UUD modified latex compositions, as described above or when used to further modify an asphalt composition, are particularly useful in the treatment or
25 coatings of roofs and/or pavement surfaces, by employing the additives disclosed herein,

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such as surfactants, pigments, fillers, wetting, agents, anti-oxidants, defoamers, adhesion promoters, u.v. stabilizers, thickening agents, biocides, anti-microbials, and the like.

The polyurethane-urea dispersion may also employ other latices. For example, the composition may employ many types of acrylics; synthetic and natural
5 rubbers; neoprenes; nitrile rubber; butyl rubber; polybutadiene; styrene-acrylic; styrene-butadiene; acrylonitrile; styrene-butadiene or styrene-isoprene block copolymers (e.g., "Kraton" by Shell Chemical); and chlorosulfonated polyethylene ("Hypalon" by duPont).

It is often desirable for ease of application to thicken the compositions of the present invention, particularly those employing a latex; in short, it may be necessary
10 or desirable to increase its viscosity. Useful thickeners for use in the compositions and methods of the present invention, include, for example, urea copolymers of polyvinyl pyrrolidone, polyacrylates, polyacrylamides, polyesterpolyols, polyether polyols, silicates, synthetic cellulose derivatives and preferably the cellulose ether derivatives, such as, for example, hydroxypropyl methylcellulose, e.g., Methocel. The thickening can also be
15 attained by the utilization of solid filler materials, such as calcium carbonates, fumed silica, clays, mica, aluminum pastes, aluminum flakes, polyolefins. Materials such as the calcined clays or hydrated alumina, which are very fine particulate powders, are compatible at up to 50% by weight of the total latex solids. At the higher concentrations of such filler materials, a mastic may be formed. Certain of the filler materials are useful as pigments
20 and include, for example, carbon black and other conventional pigments which provide a white or other color to the final resin film. For use as a pigment, generally only from about 0.5 to about 15% by weight is necessary. The pigments or fillers are preferably added as dispersions, either in aqueous or non-aqueous systems. The non-aqueous systems, are generally, preferably, at least partially miscible in water. If desired, however,
25 the particulate material can be added directly as a powder.

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Stabilizers against discoloration and aging, such as any of the well known antioxidants and ultraviolet screening materials can also be employed in the compositions and methods of the present invention as desired for the particular purpose for which a film is to be used. Plasticizing agents can also be utilized, such as the phosphate esters, 5 which, in addition to their plasticizing activity also act as emulsifiers, especially in combination with the alkoxyated alkylphenols. Biocides and/or antimicrobials may also be employed.

The final UUD preferably contains from about 25 to 70% by weight of solids in water and most preferably from about 30% to about 65% by weight of solids. 10 The preferred average particle size for UUD's of the present invention is as express about, i.e., less than one micron; in one highly preferred embodiment the preferred average particle size are in the range of between about 0.02 and about 0.06 microns. This relatively small particle size (less than one micron) is important in that, among other benefits, it gives rise to dramatically better performance, especially when used as a 15 modifier of asphalt and/or latex, chalky and/or flexible surfaces.

The latices which are obtained in accordance with the present invention are generally stable at ambient temperatures, and can be used to produce films, for instance, which have reproducible, consistent properties, including especially water resistance and adhesion.

20 The following are examples of the products and the processes for preparing said products according to this invention. The examples are not intended to be exclusive of the full scope of this invention, but merely set out certain preferred embodiments thereof.

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EXAMPLE GROUP A

EXAMPLE A-1

Preparation of a UUD

5 Poly(oxypropylene)glycol (PPG, MW=2000) 100 parts (by wt.), demoistured at 80°-90°C under vacuum for about 10 hours, is added in a reaction kettle equipped with electrical stirrer, thermometer, dry nitrogen inlet and heating jacket. Dimethylolpropionic acid (DMPA) 6.7, N-methylpyrrolidone (NMP) 14.6 and dibutyltin dilaurate (T12) 0.05% (based on the total weight of prepolymer) is then added to above reaction kettle and
10 heated to 60° ± 5°C with stirring under dry nitrogen for about 5-10 min. until a uniform mixture was formed. Biscyclohexylmethane-4, 4'-diisocyanate (H₁₂MDI) 39.3g is then added and the reaction of preparing the pendant carboxylic acid - containing polyurethane (PU) prepolymer was carried out at 85° - 90°C for 3-4 hr. with stirring under dry nitrogen until the NCO content of the prepolymer was close to the theoretical calculation
15 according to the titration of n-dibutylamine. The temperature is decreased to about 70°C and triethylamine (TEA) 10.1g is added. The neutralization between the pendant carboxylic acid of PU prepolymer and the tertiary amine of TEA is carried out at about 70°C for 30-40 min. After the temperature is decreased to about 45°C, a certain amount of distilled water (based on about 35% solids) is added under vigorous agitation to carry
20 out the dispersion of the neutralized PU prepolymer in water. The chain extension is carried out at room temperature under vigorous agitation by adding hydrazine (HZ) 1.6g or ethylenediamine (EDA) 3.0g, which is diluted with water to about 50% solids, in the neutralized prepolymer dispersion. The final product is typically a translucent dispersion with 32% solids, 70-80 cps/RT and pH = 7.5-8.0. The dispersion is cast in a glass mold
25 which is coated with a release agent at room temperature ("RT"). After the dried film is formed at RT it is put in oven at 50-60°C overnight before testing the properties.

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EXAMPLE A-2

Preparation of a UUD

The preparation and equipment are same as that described in Example A-1
5 except that PPG (MW=1000) 100g, DMPA 13.4g, NMP 19.2g, H₁₂MDI 78.6g and 0.05%
of T12 are used to prepare PU prepolymer; TEA 20.2g as well as HZ 3.2g are used to
carry out both dispersion and chain extension. A transparent polyurethane ("PU")
dispersion is obtained and a dried film is formed for testing. Both tensile strength and
modulus increased but elongation decreased when the concentration of COOH or DMPA
10 was increased.

EXAMPLE A-3

Preparation of a UUD

The preparation and equipment are same as that described in Example A-1
15 except that PPG (MW=1000) 100g, DMPA 13.4g, NMP 19.2g, IPDI 66.6g and 0.05% of
T12 are used to prepare PU prepolymer and TEA 20.2g as well as HZ 3.2g are used to
carry out both dispersion and chain extension. A transparent PU dispersion was obtained
with 35% solids and pH=7-8. Dried films were then prepared in the manner described
in Example A-1 for testing mechanical properties. As the temperature of the dispersion
20 was increased above room temperature the tensile strength and modulus decreased
although elongation increased.

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EXAMPLE A-4

Preparation of a UUD

The preparation and equipment are same as that described in Example A-1
5 except that PPG (MW=2000) 100g, DMPA 6.7g, NMP 13.3g, toluene diisocyanate (TDI)
26.1g are reacted at 80° - 85°C for about 2 hr. with no catalyst under dry nitrogen. The
PU prepolymer 146.1g is added to a container which contains both water and TEA(10.1g)
at room temperature under vigorous agitation to carry out both neutralization and
dispersion. Hyrazine (HZ, 1.6g) diluted with water is slowly added in the above
10 neutralized prepolymer dispersion under vigorous agitation to carry out the chain
extension at room temperature. A translucent PU was obtained with 30-35% solids,
pH=7-8. Dried films were then prepared for the measurement of properties.

EXAMPLE A-5

15 Preparation of a UUD

The preparation and equipment are the same as that described in Example
A-1 except that PTMG (poly(oxytetramethylene)glycol) (MW=2000) 100g, DMPA
6.7g, NMP 13.3g, toluene diisocyanate (TDI) 26.1g is reacted at 80° - 85°C for about 2 hr
20 with no catalyst under dry nitrogen. The dispersion and chain extension may be carried
out by the three methods as shown below:

Method 1. The prepolymer is neutralized with TEA at first and then
dispersed in water containing HZ to carry out both
25 dispersion and chain extension.

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Method 2. The prepolymer is neutralized and dispersed in water containing TEA. HZ is then added to carry out chain extension.

Method 3. The prepolymer is neutralized, dispersed and chain-
5 extended in water containing TEA and HZ.

Dried films are then prepared for testing purposes. The mechanical properties of this UUD are better than one's of Example A-4. The UUD of Example A-4 may also be blended with this UUD at various ratios.

10

EXAMPLE A-6

Preparation of a UUD

The preparation and equipment are the same as that described in Example A-1 except that PPG (MW=2000) 150g, DMPA 10.1g, TEA 7.6g, Hz 3.2g, NMP 17.2g
15 was used; the typical (for these examples) NCO/OH ratio of 1.5 and NCO/NHz ratio of 1.0 were also employed.

EXAMPLE GROUP B

EXAMPLE B-1

20

Preparation of UUD-Modified Acrylic dispersions

The UUD of Example A-2 is blended with various acrylic dispersions at 50/50 (based on solids) ratio at room temperature in a container under agitation until a homogeneous dispersion was formed. The dispersion blends are cast in the release agent
25 coated mold at room temperature and the film after being dried at room temperature is kept in oven at 50 - 60°C for about 15 hrs. until water or some co-solvent is completely

- 25 -

removed from the film. The sample films are aged at room temperature for one or two days before testing the properties. The appropriate curing condition for the sample films is typically room temperature for one week and 80°C for one day.

Alternatively, a ratio of about 30 parts to about 50 parts of UUD (by weight of solids) is employed.

These UUD modified acrylic dispersions, exhibit very good adhesion to chalky surfaces of weathered PIB (polyisobutylene rubber).

10

EXAMPLE B-2

Preparation of UUD-Modified styrene-acrylic dispersions.

15

The UUD of Example 2 is blended with a highly preferred styrene-acrylic dispersion RES 1019 or 10526 (by Unocal Polymers) by using same procedure as that described in Example B-1. The blends from RES 1019 typically have better properties than one from RES 10526.

20

EXAMPLE GROUP C

Three properties of a sealant are very important: Tensile strength, elongation and retention of elongation properties at low temperatures. In the examples below, to be satisfactory, the elongation capacity should be greater than 80%; tensile strength should exceed 200 psi.

25

EXAMPLE C-1

Mixtures of an anionic asphalt and a UUD from Example A-2 are made as follows. The asphalt emulsion is added relatively slowly, with agitation, to the required amount of UUD. Mixtures are made slowly, and a number of samples are

- 26 -

prepared with increasing percentages of UUD from 0 to 50%, or the desired percentage. It is important to add the asphalt to the UUD. They are then applied at a thickness of about 0.010 inches to silicone coated release paper, allowed to cure at room temperature for two days and then at 60°C for two days. Then tensile properties of the dried film are

5 determined.

To test for elongation capacity at low temperatures, a bend test is run. A bend test was made by applying about .010 inches of the 0, 30 and 50% UUD: asphalt (by solids) composition to aluminum panels. Cured as above, they are then immersed in a dry ice bath at -20° for 5 min and immediately bent at 180°C.

10 The results show that the cured asphalt emulsion has a tensile strength of only about 8 psi, while all the mixtures of asphalt and UUD have satisfactory tensile properties. The elongation capacities of mixtures with more than 20% of the UUD were satisfactory, with 30% being the preferred amount for roofing use, 50% for uses requiring very high tensile strengths such as traffic bearing waterproofing membranes.

15 In the bend test, the asphalt failed while the 30 and 50% UUD:Asphalt showed satisfactory results.

EXAMPLE C-2

Mixtures are made using the higher elongation UUD of Example A-6.

20 Mixing, curing and testing were the same as Example C-1. The 180° bend test results show that at 20, 30 and 50% UUD satisfactory results are obtained. At 20, 30 and 50% UUD, the results are also satisfactory. With this UUD, 20% is the preferred ratio.

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EXAMPLE C-3

Mixtures using a UUD made with a TDI base (Example A-4) are prepared. Mixing procedures, coating, curing and testing procedures are the same as those shown in Example C-1 (absent the bend test). Mixtures from 10 to 100% UUD are tested. It is found that levels as low as 10% UUD gave good elongation, while 20%-30% would be the preferred UUD concentration.

EXAMPLE D

10 A test can be run to determine the wetting properties and resistance to rutting of pavements made with the addition of UUDs as compared with an unmodified asphalt emulsion, even when employed at very low levels. The UUD is made with IPDI (example No. A-3). The asphalt emulsion can be made with high penetrative asphalt for use with chip seal pavements.

15 A mixture of graded aggregates is mixed with 8% by weight of:
a mixture of UUD (1.6%) and an asphalt emulsion (6.4%)

The mixtures are compacted in a cylinder required for the split tensile and Marshall tests. The mixed material is much better wetted than the asphalt only. The addition of the UUD (1.6%)/asphalt emulsion (6.4%) wets the aggregate more thoroughly.

20 The cylinders are then aged 2 days at 50°C and force is applied to the warm cylinders. The results are shown in the table that follows:

	<u>Asphalt Type</u>	<u>Split Tensile</u>	<u>Marshall Test</u>	
		Pounds	Deflection	Pounds
25	Unmodified	68	0.18	830
	Modified	544	0.40	3750

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The results of the Marshall test are especially important. Ordinarily, with hot asphalt (not an emulsion) the Marshall test will run between 2000 and 3000 pounds.

The excellent results appear to be due to the improvement in the wetting of the aggregate by the asphalt emulsion.

5

EXAMPLE GROUP E

TYPICAL FORMULATIONS

- 10 A: UUD, parts by weight of solids
 B: Latex, parts by weight of solids
 C: Asphalt emulsion, parts by weight of solids

			A	B	C
15	Example	E-1	5	0	95
		E-2	10	0	90
		E-3	20	0	80
		E-4	30	0	70
		E-5	40	0	60
20	E-6	50	0	50	
	E-7	60	0	40	
	E-8	70	0	30	
	E-9	80	0	20	
	E-10	90	0	10	
25	E-11	5	5	90	
	E-12	85	5	10	
	E-13	5	85	10	
	E-14	10	10	80	
	E-15	15	15	60	
30	E-16	25	25	50	
	E-17	20	40	40	
	E-18	40	20	40	
	E-19	35	35	30	
	E-20	90	5	5	
35	E-21	5	95	0	
	E-22	95	5	0	
	E-23	50	50	0	
	E-24	30	70	0	
	E-25	70	30	0	
40	E-26	3	97	0	
	E-27	3	0	97	
	E-28	1.5	1.5	97	

EXAMPLE GROUP F

Various novel blends and modified asphalt emulsions were prepared as follows:

1. UUD with acrylic latex (1019)
2. UUD with natural latex (NR)
- 5 3. UUD, acrylic and natural latex (NR)
4. UUD or novel blends modified asphalt emulsion

The blending process was carried out at room temperature by using a stirrer with variable speed for about 10 min. until a homogeneous mixture was formed. The UUD used is from Example A-1 unless otherwise noted.

10

TABLE 1

Table 1 shows the properties of UUD-acrylic latex (1019) with various blending ratios. The UUD is made by using IPDI and the results indicate that the tensile strength of blends is generally increased with an increasing concentration of UUD. However, the
15 elongation of blends did not change except for the 80/20 ratio. All blends with different ratios are homogeneous. The results imply that one can change tensile strength without affecting elongation of blends.

TABLE 2

20 Table 2 shows the properties of blends which are made by using UUD and acrylic 1019. However, the UUD is made by H₁₂MDI and dipropylene glycol monoether acetate (DPMA) as a replacement of "NMP". The results indicate that the tensile strength of the blends increase with increasing amounts of UUD, but elongation decreases with increasing UUD.

25

TABLE 3

Some general properties of UUD-NR blends are shown in Table 3. Three types of natural latex ("NR") are used and the properties of both NR and blends before and after heating age are shown. Both tensile strength and elongation of blends with 50/50 ratios
30 (on solids) increase by introducing UUD, compared to the properties of NR itself. Elongation of blends decrease about 10% after heating age. This suggests that an antioxidant should be introduced to avoid the oxidation of NR.

- 30 -

TABLE 4

IPDI based UUD is blended with NR at various ratios as shown in Table 4. The results indicate that the tensile strength of the blends decrease with increasing NR. Elongation also decreases except for 60/40 ratio.

5

TABLE 5

Two types of asphalt emulsion are modified by UUD at various ratios (on solids) as shown in Table 5. Asphalt A is a hard type with a low penetration degree and asphalt B apparently is a soft type with a high penetration degree. The acidic clay inside asphalt B resulted in a compatibility problem with UUD. A pretreatment of asphalt B with triethanolamine (TEAL) is carried out to improve both tensile strength and elongation (see Table 5. 70/30 ratio). With increasing amounts of TEAL elongation increases but tensile strength decreases (see Table 5 80/20 ratio). Both tensile strength and elongation of UUD modified asphalt emulsion increase with increasing amounts of UUD.

15

TABLE 6

The properties of various blends and blends modified asphalt emulsion are shown in Table 6. NR/UUD (50/50) exhibits higher tensile strength but lower elongation compared to NR/UUD/1019 (30/40/30). UUD modified asphalt (20/80) showed higher tensile strength but low elongation compared to acrylic latex 1019/asphalt (20/80). NR/UUD (6/8/6/80) show higher elongation and tensile strength compared to NR/UUD/asphalt.

20

TABLES 7 AND 8

The UUD modified asphalt emulsion (20/80) exhibits excellent low temperature impact strength compared to 1019 modified asphalt. (see Tables 7 and 8.)

25

TABLE 9

Various types of asphalt emulsions are modified by UUD at a 20/80 ratio (UUD/asphalt) as shown in Table 9. Five parts of either Triton 101 or TEAL (based on 100 parts of asphalt) are used to pretreat the asphalt emulsion. All modified asphalt emulsions show excellent properties, especially the asphalt emulsion from Hy-Grade Corp.

30

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TABLE 10

The properties of various modified asphalt emulsions based on the Hy-Grade Corp. product are shown in Table 10. Formulations 1-3 are based on 90% (solids) of asphalt and 4-8 are based on 80% of asphalt. All modified asphalt emulsions show good tensile strength and elongation before and after heating age except formulations 5 and 7, which show low elongation after heating age. All modified asphalt emulsions based on acrylic latex 1019 fail a 180° bending test (at -20°C) and all modified asphalt emulsions based on UUD pass the bending test except formulations 2 and 3, which contain UUD concentrations which appear to be too low for this particular application.

TABLE 11

The properties of NR/UUD (Example A-3 based on IPDI) before and after heating and aging are shown in Table 11. The results indicate that the tensile strength of blends increase and elongation decreases about 2-3% from the original value after heat aging.

TABLE 12

Two types of asphalt emulsions (from Japan; see Table 16) are modified by two blends, one is UUD/1019 and another is UUD/NR/1019. The properties before and after heat aging are shown in Table 12. The results indicate that DP asphalt is better than F1 asphalt and UUD1/1019 show better properties than UUD/NR/1019 after heat aging.

TABLE 13

Asphalt emulsion from Hy-Grade Corp. is modified by UUD, NR, UUD/NR and UUD/acrylic latex/1019 as shown in Table 13. After heat aging, both modified asphalt emulsion based on NR and UUD/NR result in very poor elongation because of oxidation of NR. However, both modified asphalt emulsions based on UUD and UUD/acrylic latex/1019 exhibit good properties after heat aging, in particular UUD/acrylic latex/1019.

TABLE 14

Asphalt emulsion with a low penetration degree (harder than Hy-Grade asphalt emulsion) is modified by UUD, NR, 1019, UUD/NR and UUD/1019 as shown in Table 14. All modified asphalt emulsions with 90% of asphalt emulsion and all modified asphalt emulsions with acrylic latex 1019 fail the 180° bending test. However, all modified asphalt

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emulsions based on UUD, NR and 80% of asphalt pass the bending test. This test is based upon U.S.T.M. test _____.

TABLE 15

- 5 Asphalt emulsions from both Hy-Grade Corp. and Japan modified by UUD or blends are listed showing 180° peel strength to chalked asphalt paper. UUD modified Hy-Grade asphalt gives high peel strength and UUD/acrylic latex/1019 modified asphalt (Japan) exhibits better peel strength.

TABLE 16

10

Various properties of useful commercially available asphalt emulsions are tested.

Table 1. Effect of various blending ratios of acrylic latex 1019 with IPDI based UUD on the mechanical properties of blends.

5	Samples*	T _g , psi	E, %
	1019/IPDI-UUD		
	80/20	444	970
	60/40	638	880
	50/50	757	840
10	40/60	941	850
	20/80	1196	850

15 * Solids content is 50% for 1019 and 28.6% for IPDI based UUD. The blending ratios are based on solids.

Table 2. Effect of various blending ratios of acrylic latex 1019 with DPMA based UUD on the mechanical properties of blends.

20

25	Samples*	T _g , psi	E, %
	1019/DPMA-UUD		
	80/20	338	1020
	60/40	597	740
	50/50	845	680
	40/60	1157	640
30	20/80	1674	590

35 * Solids content is 50% for 1019 and 36.7% for DPMA (dipropylene glycol monoether acetate) based UUD. The blending ratios are based on solids.

Table 3. Effect of various natural latices and blends of natural latices with UUD on the mechanical properties before and after heat aging.

5	Sample	T_g , psi	E, %
	NR407	372	840
	NR411	376	810
	NR358	292	980
	NR407/UUD (50/50)	1198	1100
10	NR411/UUD (50/50)	1436	1060
	NR358/UUD (50/50)	1499	1100
	After 60°C x one weeks		
	NR 407	190	850
	NR 411	307	1000
15	NR 358	308	1100
	NR407/UUD (50/50)	1400	950
	NR411/UUD (50/50)	1294	880
	NR358/UUD (50/50)	1480	920
	After 60°C x two weeks		
20	NR 407	130	720
	NR 411	207	890
	NR 358	101	660
	NR407/UUD (50/50)	1357	840
	NR411/UUD (50/50)	1503	850
25	NR358/UUD (50/50)	1416	900

Table 4. Effect of various blending ratios of NR/IPDI-UUD on the properties of blends.

	NR/IPDI-UUD*	T _g , psi	E, %
5	0/100	2487	820
	50/50	1000	810
	60/40	929	850
	70/30	366	650
	80/20	236	660
10	100/0	297	980

* IPDI based UUD.

Table 5. Effect of various blending ratios of UUD asphalt emulsions on the mechanical properties of blends

	Sample	TEAL, % ¹⁾	T _g , psi	E, %
	Asph. A/UUD²⁾			
	100/0	0	170	189
25	90/10	0	164	367
	80/20	0	250	541
	70/30	0	477	678
	Asph. B/UUD			
	100/0	0	63	150
30	90/10	5	92	1163
	80/20	3	263	811
	80/20	6	184	1140
	70/30	0	325	360
35	70/30	3	366	680

- 1). Based on asphalt emulsion. TEAL - Triethanolamine
- 2). Based on solids. Both asphalt A and B are made by a Japanese company.

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Table 6. Effect of various blends and blending ratios on the mechanical properties of blends

Blends	T _g , psi	E, %
NR (En 407)	195	770
NR (A-Line)	316	760
NR(En407)/UUD (50/50)	1206	780
NR(En407)/UUD/1019 (30/40/30)	538	870
UUD/Asph. (20/80)	218	440
1019/Asph. (20/80)	80	900
NR(En407)/UUD/Asph. (10/10/80)	163	560
NR(En407)/UUD/1019/Asph. (6/8/6/80)	158	620

Note:

NR (En 407) and NR (A-Line): From Ennar Latex, Inc. about 61% solids.

UUD:UUD was prepared by using DPMA as solvent.

Asph.:Asphalt emulsion with about 58% solids and pH is greater than 7.

All blending ratios are based on solids. The samples were dried at room temperature for two days and in oven at 60°C for 24 hours before test.

Table 7. Comparison of low temperature impact strength between UUD and acrylic latex (1019) modified asphalt emulsions

Sample	Indirect Impact Strength, lb in.			
	12	24	32	36
UUD/asph. (20/80)	P	P	P	P
1019/asph. (20/80)	F	F	F	F

* The aluminum panel with modified asphalt was immersed in a -20°C cold bath for 5 min. before testing. (P - pass, F - fail).

Table 8. Comparison of flexibility between UUD and acrylic modified asphalt emulsions*

5	Sample	After 180° bending test
	UUD/asph. (20/80)	Smooth surface no cracking
	UUD/1019/asph. (10/10/80)	partial cracking on the surface
	1019/asph. (20/80)	Significant cracking on the surface

10 * The aluminum panel with modified asphalt was immersed in a -20°C cold bath for 5 min. before 180° bending.

15 Table 9. Effect of various asphalt emulsions on the properties of UUD modified asphalt emulsion

20	Asphalt emulsion	T _g psi	E, %
	RPM asphalt (with #101)	264	536
	FC asphalt (with #101)	298	480
	FC asphalt (with TEAL)	355	490
	DP asphalt	288	330
	Hy-G asphalt (first)	573	540
25	Hy-G asphalt (SSI-HH)	561	530

Basic formulations - See Table 16

Table 10. Mechanical properties of HY-G asphalt emulsion modified by UUD, NR and acrylic latex 1019

5	Formulation	1	2	3	4	5	6	7	8
	Asphalt	90	90	90	80	80	80	80	80
	UUD	10	5	5	20	-	-	10	10
	NR	-	5	-	-	20	-	10	-
10	1019	-	-	5	-	-	20	-	10
	Properties								
	T _g , psi	144	105	98	312	137	168	149	206
	E, %	510	760	550	570	540	660	540	530
15	180° Bending at -20°C	P	F	F	P	P	F	P	P
	70°C x one week								
	T _g , psi	131	150	111	246	135	130	140	177
20	E, %	780	770	1020	730	240	1280	370	1040

(P - Pass, F - Fail)

Table 11. Effect of various blending ratios of NR/IPDI-UUD on the properties of blends

30	NR/IPDI-UUD*	T _g , psi	E, %	T _g , psi	E, %
		(Before heat and aging)		(60°C x one month)	
	50/50	1147	1050	1040	800
	60/40	709	940	924	860
	70/30	483	870	617	810
	80/20	327	790	606	900
35	90/10	300	900	248	790

* IPDI based UUD

Table 12. Effect of heat aging on the properties of modified asphalt emulsion (Heat aging conditions: 60°C x 6 days + 80°C x 1 day)

5

10

15

Composition	DP Asphalt		FL asphalt	
	Ts, psi	E, %	Ts, psi	E, %
Asph/UUD/1019				
80/10/10	223(239)	400(380)		
60/20/20	363(400)	480(530)	194(165)	560(470)
40/30/30	535(515)	670(610)	374(338)	740(590)
Asph/UUD/NR/1019				
80/10/5/5	209(236)	360(280)	71(87)	450(320)
60/20/10/10	368(330)	500(380)	176(193)	660(530)
40/20/20/20	439(338)	680(570)	269(170)	770(540)

*

The properties after heating aging are shown in the bracket

Table 13. Effect of heat aging on the properties of modified Hy-G asphalt emulsion
(Heat aging conditions: 60°C x 21 days + 80°C x 1 day)

5

Samples	Before heat aging		After heat aging	
	T _g , psi	E, %	T _g , psi	E, %
Asph./UUD/NR				
(90/5/5)	105	760	243	<10
(80/10/10)	149	540	207	<10
Asph./NR				
(80/20)	137	540		<10
Asph./UUD				
(90/10)	144	510	176	500
(80/20)	312	570	257	420
Asph./UUD/1019				
(90/5/5)	98	550	130	570
(80/10/10)	206	530	248	580

20

Table 14. Effect of various modified asphalt emulsions on 180° bending test (at -20°C)

Sample	Edge surface after bending	Failure
UUD/asph (10/90)	Cracking	Failure
UUD/NR/asph (5/5/90)	Cracking	Failure
UUD/1019/Asph (5/5/90)	Cracking	Failure
UUD/asph (20/80)	No cracking	Pass
NR/asph (20/80)	No cracking	Pass
1019/asph (20/80)	Cracking	Failure
UUD/1019/asph (10/10/80)	Cracking	Failure
UUD/NR/asph (10/10/80)	No cracking	Pass

* The modified asphalt emulsion is coated on a standard steel panel by using a doctor blade. After one week at RT the sample panel is immersed into a dry ice/acetone/water bath for 5 to 10 min. The sample panel is then taken out to carry out 180° bending test immediately.

Table 15. Effect of various modified emulsions on the peel strength of the modified asphalt emulsions to chalked asphalt paper

Sample	Hy-G asphalt 180° peel strength, lb in.	Japan asphalt 180° peel strength, lb in.
UUD/asph (20/80)	4.26	5.08
1019/asph (20/80)	3.37	5.15
1019/UUD/asph (10/10/90)	3.3	5.46
UUD/1019 (20/80)	2.13	-
1019 (100)	1.77	-

Table 16. Properties of various commercial asphalt emulsions

5	Asphalt emulsion	Solids, %	pH	Type	Penetration
	RPM (USA)	50	6.5-7	Nonionic	
	FL (Japan)	58.4	7-8	Anionic	
	DP (Japan)	58	<7	Cationic	
	HY-G1 (USA)	61.9	>7	Anionic	
10	HY-G2 (USA)	65.2	>7	Anionic	

TABLES 17 AND 18

15

Tables 17 and 18 demonstrate the importance of particle size of the UUD in the compositions and methods of the present invention. The IPDI based UUD modified natural latex (NR) or asphalt emulsions exhibited better properties tensile strength (T_s) and elongation (E) than H_{12} MDI based UUD modified NR or asphalt. This is due to the

20 fact that the particle size of the UUD plays an important role in the fixed property of UUD modified latex or asphalt.

Table 17. Effect of particle size in UUD on the properties of modified natural latex.

25	Sample	UUD	UUD particle size	UUD/NR	T_s , psi	E, %
	1	H_{12} MDI	0.6 μ	60/40	1083	600
	2	H_{12} MDI	0.6 μ	50/50	248	1060
	3	H_{12} MDI	0.06 μ	40/60	536	490
	4	IPDI	0.04 μ	60/40	1205	880
30	5	IPDI	0.04 μ	50/50	914	900
	6	IPDI	0.04 μ	40/60	618	914

*) Based on solids

Table 18. Effect of particle size of UUD on the properties of modified asphalt emulsion.

5

Sample	UUD ¹⁾	UUD particle size	Asphalt ²⁾	T _g , psi	E, %
1	H ₁₂ MDI	0.6μ	R2	146	450
2	H ₁₂ MDI	0.6μ	M2	149	280
3	H ₁₂ MDI	0.6μ	H-HH	222	540
4	H ₁₂ MDI	0.6μ	K-SS	141	560
5	H ₁₂ MDI	0.6μ	K-noil	46	420
6	H ₁₂ MDI	0.6μ	K-CSS	51	410
7	H ₁₂ MDI	0.6μ	E-1	96	410
8	IPDI	0.04μ	R2	198	660
9	IPDI	0.04μ	M2	223	450
10	IPDI	0.04μ	H-HH	277	690
11	IPDI	0.04μ	K-SS	220	780
12	IPDI	0.04μ	K-noil	90	890
13	IPDI	0.04μ	K-CSS	66	810
14	IPDI	0.04μ	E-1	135	860

1) Aliphatic diisocyanate used in the preparation of UUD.

2) The properties of asphalt emulsion are as follows:

25

R2 -	70% solids	pH=12-13
M2 -	53.9%	
H-HH -	67.4%	
K-S -	63%	pH=12
K-noil -	68%	pH=7
K-CSS -	63%	pH=2
E-1 -	63%	

30

35 The modified asphalt emulsion was based on the following basic formula (on solids):

40

Asphalt emulsion	100
UUD	100
Acrylic latex	20
Nolonic surfactant	17
Carbon black dispersion	5

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CLAIMS

What is Claimed is:

1. An improved coating or sealing composition comprising a water borne asphalt emulsion which has been modified by the inclusion of a urea urethane dispersion wherein said urethane urea dispersion has an average particle size of less than about one micron.
2. The coating composition according to claim 1 wherein said urethane urea dispersion is anionic.
3. The coating composition according to claim 1, wherein said urethane urea dispersion is cationic.
4. The coating composition according to claim 1, wherein said urethane urea dispersion is nonionic.
5. The coating composition according to claim 1, wherein said asphalt emulsion further comprises at least one additive.
6. The coating composition according to claim 5, wherein said additive is selected from a group consisting of wetting agents, antioxidants, defoamers, adhesion promoters, u.v. stabilizers, thickening agents, and mixtures thereof.
7. An improved coating composition comprising a water borne asphalt emulsion modified by the addition of a urethane urea dispersion-modified latex, wherein said urethane urea dispersion has an average particle size of about one micron.

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8. The coating composition according to claim 7, wherein said urethane urea dispersion is anionic.

9. The coating composition according to claim 7, wherein said
5 urethane urea dispersion is cationic.

10. The coating composition according to claim 7, wherein said urethane urea dispersion is nonionic.

10 11. The coating composition according to claim 7, wherein said latex is selected from a group consisting of acrylic latices, natural latices, synthetic latices, vinyl-based latices, epoxy-based latices, neoprene-based latices, natural rubber-based latices, chloro sulfinate vinyl-based latices, butyl rubber-based latices, ethylene-propylene-isoprene (diene) copolymer modified latices, and mixtures thereof.

15 12. The coating composition according to Claim 7, wherein said asphalt emulsion further comprises at least one additive.

13. The coating composition according to Claim 12, wherein
20 said additive is selected from a group consisting of wetting agents, antioxidants, defoamers, u.v. stabilizers, adhesion promoters, thickening agents and mixtures thereof.

14. A coating composition according to claims 1, 2, 3, 4, 5, 6,
7, 8, 9, 10, 11, 12 or 13 wherein said urethane urea dispersion is present at a level of
25 about 1 to about 90 percent, by weight of solids.

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14. A coating composition according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13 wherein said urethane urea dispersion is present at a level of about 10 to about 90 percent, by weight of solids.
- 5 15. A coating composition according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13 wherein said urethane urea dispersion is present at a level of about 30 to about 50 percent, by weight of solids.
- 10 16. A method of applying a protective coating to a surface in need of such coating comprising applying a composition prepared according to claims 1 or 7 and allowing said composition to cure.
- 15 17. A method of applying a protective coating to a surface in need of such coating comprising applying a composition which includes a water borne urethane urea dispersion wherein said urethane urea dispersion has an average particle size of about 0.65 microns and is present at a level of up to about 90% by weight of solids.
- 20 18. A method of applying a coating composition according to Claim 17, wherein said urethane urea dispersion is anionic.
19. A method of applying a coating composition according to Claim 17, wherein said urethane urea dispersion is cationic.
- 25 20. A method of applying a coating composition according to Claim 17, wherein said urethane urea dispersion is nonionic.

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21. A method of applying a coating composition according to Claim 17, wherein said urethane urea dispersion is H₁₂MDI-based.
22. A method of applying a coating composition according to
5 Claim 17, wherein said urethane urea dispersion is IPDI-based.
23. A method of applying a coating composition according to Claim 17, wherein said urethane urea dispersion is TDI-based.
- 10 24. A method of applying a coating composition according to Claim 17, wherein said composition is applied to a roof.
25. A method of applying a coating composition according to Claim 17, wherein said composition is applied to a chalky surface.
15
26. A method of applying a coating composition according to Claim 17, wherein said composition is applied to a paved surface.
27. A method of applying a protective coating to a surface in
20 need of such coating, comprising applying a composition containing a latex wherein said latex containing composition is modified by the inclusion of an urethane urea dispersion according to claims 18, 19, 20, 21, 22, or 23, and wherein said urethane urea dispersion is present in said composition at a level of up to 95%, by weight of solids.
- 25 28. A method of applying a coating composition according to Claim 27, wherein said latex further comprises at least one additive.

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29. A method of applying a coating composition according to Claim 28, wherein the latex is selected from the group consisting of acrylic latices, natural latices, synthetic latices, vinyl-based latices, epoxy-based latices, neoprene-based latices, natural rubber-based latices, chloro sulfinate vinyl-based latices, butyl rubber-based latices, ethylene-propylene-isoprene (diene) copolymer modified latices, and mixtures thereof.
- 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/02800

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08J 3/00; C08K 3/20, 5/01; C08L 95/00, 91/08

US CL :524/60, 61, 62, 705, 839

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; AQUEOUS OR WATER, URETHANE?, POLYURETHANE?, ISOCYANATE?, DIISOCYANATE?, POLYISOCYANATE?, BITUMEN?, ASPHALT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,645,945 (LESENE ET AL.) 29 February 1972, See entire document.	1-29
Y	US, A, 4,724,245 (LALANNE ET AL.) 09 February 1988, See entire document.	1-29
Y	US, A, 3,967,012 (EBNER) 29 June 1976, See entire document.	1-29
Y	US, A, 4,403,083 (MARANS ET AL.) 06 September 1983, See entire document.	1-29
Y	US, A, 4,160,065 (LOEWIG KEIT ET AL.) 03 July 1979, See entire document.	1-29

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

06 JULY 1992

Date of mailing of the international search report

03 AUG 1992

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